

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 01 May 2000 (01.05.00)	
International application No. PCT/CA99/00804	Applicant's or agent's file reference T8465218WO
International filing date (day/month/year) 03 September 1999 (03.09.99)	Priority date (day/month/year) 04 September 1998 (04.09.98)
Applicant OSMAN, Akhtar et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
01 April 2000 (01.04.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer Pascal Piriou Telephone No.: (41-22) 338.83.38
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PATENT COOPERATION TREATY

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NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

NASSIF, Omar, A.
Gowling Lafleur Henderson LLP
Suite 4900
Commerce Court West
Toronto, Ontario M5L 1J3
CANADA

Date of mailing (day/month/year)
23 August 2000 (23.08.00)

Applicant's or agent's file reference
T8465218WO

International application No.
PCT/CA99/00804

IMPORTANT NOTIFICATION

International filing date (day/month/year)
03 September 1999 (03.09.99)

1. The following indications appeared on record concerning:

☐ the applicant ☐ the inventor ☒ the agent ☐ the common representative

Name and Address

NASSIF, Omar, A.
Gowling, Strathy & Henderson
Suite 4900
Commerce Court West
Toronto, Ontario M5L 1J3
Canada

State of Nationality

State of Residence

Telephone No.

416-862-5775

Facsimile No.

416-862-7661

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person ☒ the name ☐ the address ☐ the nationality ☐ the residence

Name and Address

NASSIF, Omar, A.
Gowling Lafleur Henderson LLP
Suite 4900
Commerce Court West
Toronto, Ontario M5L 1J3
Canada

State of Nationality

State of Residence

Telephone No.

416-862-5775

Facsimile No.

416-862-7661

Teleprinter No.

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

☒ the receiving Office ☐ the designated Offices concerned
☐ the International Searching Authority ☒ the elected Offices concerned
☒ the International Preliminary Examining Authority ☐ other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

I. Britel

Telephone No.: (41-22) 338.83.38

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference T8465218W0	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/CA 99/ 00804	International filing date (day/month/year) 03/09/1999	(Earliest) Priority Date (day/month/year) 04/09/1998
Applicant BAYER INC. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

CT/CA 99/00804

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F136/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 109 082 A (MATSUDA TERUHIKO ET AL) 28 April 1992 (1992-04-28) column 3, line 56 - line 62; claims ---	1-30, 32
X	SMIRNOVA L V ET AL: "BUTADIENE POLYMERIZATION WITH A COBALT SALT-DIISOBUTYLALUMINUM CHLORIDE-WATER CATALYTIC SYSTEM AT LOW TEMPERATURE" POLYMER SCIENCE: SERIE A,US,INTERPERIODICA, vol. 38, no. 3, page 274-278 XP000591727 ISSN: 0965-545X abstract; page 277, left column, lines 10-13 and lines 43-46 --- -/--	1-30, 32

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

15 December 1999

Date of mailing of the international search report

22/12/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Humbeeck, F

INTERNATIONAL SEARCH REPORT

International Application No

T/CA 99/00804

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 397 851 A (KNAUF THOMAS F ET AL) 14 March 1995 (1995-03-14) cited in the application column 6, line 1 - line 17; claims ---	1-30, 32
A	EP 0 258 924 A (SHELL INT RESEARCH) 9 March 1988 (1988-03-09) claim 1 -----	31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 99/00804

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5109082	A	28-04-1992	JP 4085304 A	18-03-1992
US 5397851	A	14-03-1995	CA 2117950 A	10-05-1995
			DE 69405683 D	23-10-1997
			DE 69405683 T	22-01-1998
			EP 0652239 A	10-05-1995
			JP 7188341 A	25-07-1995
EP 0258924	A	09-03-1988	US 4730071 A	08-03-1988
			AU 603370 B	15-11-1990
			AU 7683887 A	18-02-1988
			CA 1296348 A	25-02-1992
			JP 63056508 A	11-03-1988

REC'D 31 OCT 2000

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference T8465218WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/CA99/00804	International filing date (day/month/year) 03/09/1999	Priority date (day/month/year) 04/09/1998
International Patent Classification (IPC) or national classification and IPC C08F136/06		
Applicant BAYER INC. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 01/04/2000	Date of completion of this report 27.10.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Adams, F Telephone No. +49 89 2399 8511 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/CA99/00804

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-12 as originally filed

Claims, No.:

1-32 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1-32
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-32
Industrial applicability (IA)	Yes:	Claims 1-32
	No:	Claims

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/CA99/00804

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/CA99/00804

Ad V:

- 1). The present application does not satisfy the requirements set forth in Article 33(2) PCT because the subject-matter of the claims is not new in respect of prior art as defined in the regulations (Rule 64(1)-(3) PCT).

US-A-5109082 (D1, cited in the Search Report) discloses the preparation of cis-1,4-polybutadiene by polymerizing 1,3-butadiene in the presence of a catalyst and an organic solvent wherein gelation is inhibited by passing water through a porous filter having a pore diameter of ≤ 5 micrometer and dispersing it in the organic solvent (cf. claims 1, 4 and 5; column 1, lines 54 to column 2, lines 46; column 2, lines 64 to column 3, lines 3; column 3, lines 56 to 62; examples 1 to 8 and comparative example 1).

The subject-matter of the claims is furthermore known from L.V. Smirnova et al, Polymer Science Ser. A, vol. 38, no. 3, page 274-278 (1996) (D2, cited in the Search Report; cf. whole document) and US-A-5397851 (D3, cited in the application; cf. claims 1 to 11; column 6, lines 1 to 17; lines 43 to 58; example 2).

Ad VIII:

- 1). Unclear expressions like "about" are not deleted throughout the claims and the description (Art. 6 PCT).
- 2). It appears to be an essential feature of the invention that the amount of water is from 0.3 to 0.8 millimols per millimol of the alkyl aluminum chloride used (cf. page 7, lines 1 to 3). This feature is not included in claim 1 (Art. 6 PCT).

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08F 136/06	A1	(11) International Publication Number: WO 00/14130 (43) International Publication Date: 16 March 2000 (16.03.00)
(21) International Application Number: PCT/CA99/00804 (22) International Filing Date: 3 September 1999 (03.09.99) (30) Priority Data: 2,246,608 4 September 1998 (04.09.98) CA (71) Applicant (for all designated States except US): BAYER INC. [CA/CA]; 1265 Vidal Street South, P.O. Box 3001, Sarnia, Ontario N7T 7M2 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): OSMAN, Akhtar [CA/CA]; Apartment 506, 495 Errol Road West, Sarnia, Ontario N7V 2B8 (CA). BARSAN, Florin [CA/CA]; 508-200 London road, Sarnia, Ontario N7T 7S9 (CA). (74) Agents: NASSIF, Omar, A. et al.; Gowling, Strathy & Henderson, Suite 4900, Commerce Court West, Toronto, Ontario M5L 1J3 (CA).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: GEL REDUCTION IN HIGH CIS-1,4-POLYBUTADIENE PRODUCTION PROCESS		
(57) Abstract A process for the production of cis-1,4-polybutadiene having a low level of gel content is described. The process comprises polymerizing 1,3-butadiene in the presence of a catalyst and a polymerization diluent. The polymerization diluent comprises an organic solvent and water particles having a median particle size less than or equal to about 10 μm . By controlling the mean particle size of the water present in the diluent, the level of gel content in the polymer product may be reduced.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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GEL REDUCTION IN HIGH CIS-1,4 POLYBUTADIENE
PRODUCTION PROCESS

TECHNICAL FIELD

5 The present invention relates to an improved process for the production of polybutadiene having a high cis-1,4 content and a reduced gel content.

BACKGROUND ART

Processes for the production of polybutadiene having a high cis-1,4
10 content, generally known cis-1,4-polybutadiene, are well known. Such processes include the polymerization of 1,3-butadiene in an inert polymerization diluent using as catalyst a mixture of a transition metal salt, such as a cobalt salt, an aluminum alkyl halide or a mixture aluminum alkyl halides and water. During such processes, same gel is produced, such gel being essentially
15 insoluble particles containing cross-linked polybutadiene. The gel is not a desirable component due to the problems it can cause to equipment used for the production of the polymer and due to the problems it can cause relating to the quality of the cis-1,4-polybutadiene.

It is thus desirable to minimize and reduce to the lowest level possible
20 the extent of gel formation during the polymerization process.

United States patent 3,094,514 teaches a process for the production of a cis-1,4-polybutadiene, having a cis-1,4-content greater than 90 per cent. Generally, the process comprises polymerization of 1,3-butadiene in a hydrocarbon diluent in the presence as catalyst of an anhydrous dihalide
25 diluent cobalt salt, a monoalkyl aluminum, and dialkyl aluminum monohalide. A similar type of process is described in United States patent 3,135,725. United States patent 3,646,001 teaches that cis-1,4-polybutadiene may be produced by polymerizing 1,3-butadiene in the presence of cobalt octoate and diethyl aluminum chloride which have been
30 reacted with benzene containing water. United States patent 4,224,426 teaches the polymerization of 1,3-butadiene to produce cis-1,4-polybutadiene

-2-

in the presence of a cobalt compound, at least one organo-aluminum chloride and water, the polymerization diluent being a mixture of C₅-C₈ cycloalkane, a saturated aliphatic hydrocarbon or an α -monoolefin, and an alkyl substituted benzene having 1 to 4 alkyl substituents. United States patent 5,397,851 teaches a process for the production of a cis-1,4-polybutadiene by the polymerization of 1,3-butadiene in an inert hydrocarbon diluent in the presence as catalyst of a diluent cobalt salt, an alkyl aluminum chloride, a tri-alkyl aluminum compound and water.

10 DISCLOSURE OF THE INVENTION

An objective of this invention is a process for the production of a high cis-1,4-polybutadiene having a very low level of gel content.

Accordingly, in one of its aspects, the present invention provides a process for the production of cis-1,4-polybutadiene having a low level of gel content, the process comprising the step of polymerizing 1,3 butadiene in the presence of a catalyst and a polymerization diluent, the polymerization diluent comprising an organic solvent and water particles having a median particle size less than or equal to about 10 μ m.

In one of its preferred embodiments, the present invention provides a process for the preparation of an essentially linear cis-1,4-polybutadiene having a very low level of gel content, the process comprising polymerizing 1,3-butadiene in the presence of a cobalt salt-organo aluminum halide-water catalyst system, the improvement being that the polymerization is carried out in the presence as polymerization diluent of a mixture of a C₅-C₆ cycloalkane and butene-1, a cobalt salt of an organic acid having 6 to 12 carbon atoms in the organic acid, an organo aluminum halide selected from (I) a mixture of (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesqui chloride and (b) an organo aluminum or formula R₃ Al wherein R is an alkyl group having 8 to 12 carbon atoms and (II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms, a polymerization modifier selected from 1,2-butadiene and 1,3-cyclo

octadiene, and water, said water having been mixed with at least a portion of said polymerization diluent such that the water is present in said polymerization diluent as particles having a median particle size less than or equal to about 10 μm .

- 5 Thus, the present inventor has discovered that controlling the median particle size of the water used in the diluent surprisingly and unexpectedly results in the production of high cis-1,4-polybutadiene having a relatively low level of gel content. Thus, the median diameter of the water particles used in the polymerization diluent is less than or equal to about 10 μm .
- 10 Preferably, the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm , more preferably from about 0.5 μm to about 6 μm , most preferably from about 1 μm to about 5 μm . The median particle size of the water particles may be determined in a conventional manner, for example, using a
- 15 Mastersizer™ particle size measuring system commercially available from Malvern Instruments Inc.

BEST MODE FOR CARRYING OUT THE INVENTION

- 20 Thus, the present process relates to the use of a polymerization diluent comprising an organic solvent and water particles.

 Preferably, the organic solvent is selected from the group comprising an aliphatic compound, an aromatic compound and mixtures thereof. The aliphatic compound may be selected from a saturated hydrocarbon, an unsaturated hydrocarbon and mixtures thereof.

- 25 Preferred saturated hydrocarbons may be selected from the group comprising $\text{C}_4\text{-C}_{10}$ aliphatic hydrocarbon, a $\text{C}_5\text{-C}_{10}$ cyclic aliphatic hydrocarbon, a $\text{C}_6\text{-C}_9$ aromatic hydrocarbon, a $\text{C}_2\text{-C}_{10}$ monoolefinic hydrocarbon and mixtures thereof.

Non-limiting examples of a suitable C₄-C₁₀ aliphatic hydrocarbon may be selected from the group comprising butane, pentane, hexane, heptane, octane and mixtures thereof.

5 Non-limiting examples of a suitable C₂-C₁₀ monoolefinic hydrocarbon may be selected from the group comprising butene-1, pentene-1, hexene-1 and mixtures thereof.

10 Non-limiting examples of a suitable C₅-C₁₀ cyclic aliphatic hydrocarbon may be selected from the group comprising unsubstituted cycloalkanes, methyl substituted cycloalkanes, ethyl substituted cycloalkanes and mixtures thereof.

Non-limiting examples of a suitable C₅-C₁₀ cyclic aliphatic hydrocarbon is selected from the group comprising cyclopentane, cyclohexane, cyclooctane and mixtures thereof.

15 Non-limiting examples of a suitable a C₆-C₉ aromatic hydrocarbon may be selected from the group comprising benzene, toluene, xylene and mixtures thereof.

The most preferred organic solvent for use in the present process comprises a mixtures of cyclohexane and butene-1.

20 Preferably, the polymerization diluent further comprises a polymerization modifier. The use of such a modifier allows for controlling the molecular weight of the polymer product. Illustrative examples of useful polymerization modifiers for use in the present process may be selected from the group comprising C₂-C₁₈ non-conjugated dienes, C₆-C₁₂ cyclic dienes and mixtures thereof. Non-limiting examples of suitable polymerization
25 modifiers may be selected from the group comprising 1,2-butadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene and mixtures thereof. The amount of polymerization modifier may be from about 1.6 to about 3.5, preferably from about 1.95 to about 3.0, millimols per mole of 1,3-butadiene in the polymerization mixture.

The choice catalyst that is employed in butadiene polymerization art are well known. Preferably, the catalyst comprises a substantially anhydrous cobalt salt and an organo-aluminum halide compound.

The substantially anhydrous cobalt salt may comprise a compound
5 having the formula CoA_m , wherein A is selected from a monovalent anion and a divalent anion, and m is 1 or 2. Preferably, the anion is derived from a $\text{C}_6\text{-C}_{12}$ organic acid. Thus, non-limiting examples of usefully such anions may be selected from the group comprising an acetylacetonate, an acetate, a hexanoate, an octoate, an oxalate, a tartrate, a stearate, a sorbate, an adipate
10 and a naphthenate.

The most preferred substantially anhydrous cobalt salt for use in the present process is cobalt octoate.

Preferably, the organo-aluminum halide compound comprises a compound having the formula:

15



wherein: R is a $\text{C}_2\text{-C}_{12}$ alkyl group, X is a halogen and $p+q$ is 3.

More preferably, the organo-aluminum halide compound is selected
20 from the group comprising a dialkyl aluminum chloride compound, an alkyl aluminum sesquichloride compound and mixtures thereof.

Even more preferably, the organo-aluminum halide compound is selected from:

(I) a mixture of: (a) an alkyl aluminum chloride selected from
25 diethyl aluminum chloride and ethyl aluminum sesquichloride (this may be achieved by a mixture containing approximately equimolar amounts of diethyl aluminum chloride and ethyl aluminum dichloride), and (b) an organo aluminum compound of formula R_3Al wherein R is $\text{C}_8\text{-C}_{12}$ alkyl group (e.g., trioctyl aluminum, tridecyl aluminum and the like); and

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(II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms (e.g., dioctyl aluminum chloride, didecyl aluminum chloride and the like).

Embodiment (I) is more preferred. In this preferred embodiment, it is especially preferred to use the organo aluminum compound of formula R_3Al is present in an amount of 0 to 1 percent by weight of the mixture of (I) and (II). The preferred organo aluminum compound of formula R_3Al comprises tri-octyl aluminum.

The preferred catalyst system for use in the present process comprises a cobalt salt selected from cobalt octoate and cobalt naphthenate, and an organo aluminum halide compound selected from: (i) a mixture of diethyl aluminum chloride and one or more of trioctyl aluminum, tridecyl aluminum and tridodecyl aluminum, and (ii) one or more of dioctyl aluminum chloride, didecyl aluminum chloride and didodecyl aluminum chloride.

In a preferred process, using cyclohexane and butene-1 as the diluent the weight ratio of butene-1 in the cyclohexane-butene-1 mixture may be from about 24 to about 40, preferably from about 24 to about 38 and most preferably from about 34 to about 36, weight percent. A preferred catalyst cobalt octoate which is used with a preferred organo aluminum halide compound which is a mixture of diethyl aluminum chloride and trioctyl aluminum, wherein the molar ratio of cobalt octoate to the total of the diethyl aluminum chloride plus trioctyl aluminum is from about 1:15 to about 1:30, preferably from about 1:15 to about 1:20 and wherein the molar ratio of chlorine in the diethyl aluminum chloride to the total aluminum in the diethyl aluminum chloride plus trioctyl aluminum is from about 0.7:1 to about 0.95:1, preferably from about 0.8:1 to about 0.9:1.

The amount of 1,3-butadiene in the 1,3-butadiene plus diluent mixture may be from about 15 to about 35, preferably from about 25 to about 35, weight percent.

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The polymerization mixture also contains water. The amount of water is from about 0.3 to about 0.8, preferably from about 0.5 to about 0.65, millimols per millimol of the alkyl aluminum chloride used. The water is mixed with at least a portion of the polymerization diluent. Accordingly, in the preferred diluent comprising cycloalkane and butene-1, the water may be mixed with cycloalkane alone, or, preferably with cycloalkane and butene-1 mixture. The mixing of the water with the polymerization diluent is such that the water as present in the polymerization diluent as particles having a median particle size equal to or less than 10 μm . Because of the very low solubility of water in hydrocarbons, including the polymerization diluents, and because of the long time to achieve a solution of water in such hydrocarbons, it is desirable for the present polymerization system to disperse the water in the polymerization diluent as very small particles to provide as high as possible a surface area to weight ratio for the particles so that interaction with the aluminum compound(s) is as efficiently as possible - this is believed to be important in reducing the amount of gel in the polybutadiene produced. The dispersion of water in the polymerization diluent may be achieved by various means such as, but not limited to, mechanical methods and sonic treatment. The improvement of the present invention is not dependent on the method used to obtain the dispersion of water in the polymerization diluent and is only dependent on the median diameter of the water particles used in the polymerization diluent being less than or equal to about 10 μm . Preferably, the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm , more preferably from about 0.5 μm to about 6 μm , most preferably from about 1 μm to about 5 μm .

The polymerization may be undertaken at a temperature of from about -10°C to about 50°C , preferably from about 5°C to about 40°C and most preferably from about 15°C to about 35°C . The polymerization process may be carried out in a batch process or in a continuous process, the continuous process being preferred. The reaction time for the

polymerization may be from about 20 to about 90 minutes, preferably from about 25 to about 60 minutes. However, the reaction time is not a critical aspect of the process and may be affected by the desired conversion of the 1,3-butadiene to polymer which may range from about 40 to about 90 percent.

The gel content of the polymer may be determined by a method in which the gel is separated from a solution of the polymer in styrene and weighed. In detail, approximately 50 g of polymer, accurately weighed, is dissolved in pure, filtered styrene to produce an approximately 4 weight percent by volume solution. The polymer-styrene mixture is shaken for 4 to 5 hours, then allowed to stand for 10 minutes and then filtered through a previously weighed filtration screen of 400 mesh. The filtration screen is then weighed again and the amount of wet gel is calculated as parts per million by weight based on the original weight of polymer used. Gel contents of less than about 250 ppm are desirable and less than about 150 ppm are more desirable and less than about 100 ppm are most desirable. In order to provide the greatest accuracy to the gel content of the polymer, normally at least three and up to 5 samples of the polymer are used to provide the corresponding number of gel content measurements.

In the following examples, the 1,3-butadiene was obtained from Union Carbide, the cyclohexane and butene-1 was Phillips pure grade and all three were passed through a column containing 4A molecular sieves followed by passage through a column containing 13X molecular sieves before use in polymerization. The 1,3-cyclooctadiene was used as a 20 weight percent solution in cyclohexane from Aldrich Chemical Company. Diethyl aluminum chloride in hexane as a 1 molar solution was from Albemarle Corporation and Akzo Nobel. Tri-octyl aluminum in heptane (20% wt.) was obtained from Albemarle Corporation as a 25.3 wt. % solution. Cobalt octoate was obtained from Mooney Chemical Inc. and used as a 6% cobalt solution in cyclohexane. Diethyl aluminum chloride was mixed with tri-octyl aluminum in sealed bottles under an inert gas in such ratios as to

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provide a solution having an average composition of $\text{Et}_{1.8}\text{Oct}_{0.3}\text{Al}_1\text{Cl}_{0.9}$ in cyclohexane which was used in all examples and is referred to as M-DEAC. Polymerization was undertaken in sealed 1 litre polymerization bottles at a temperature of 27°C for 40 minutes at the end of which time the
5 polymerization was stopped by the injection of 5 ml of ethanol containing required amount of stabilizer and the polymer was recovered by steam coagulation.

Embodiments of the present invention will be illustrated with reference to the following Examples which should not be used to limit or
10 construe the scope of the invention.

EXAMPLE 1

Using 1 liter glass bottles capped with gasketed crown caps, 110 g of cyclohexane, 80 g of 1,3-butadiene, 60 g of butene-1, 1.8 mL of a 20%
15 solution of 1,3-octadiene in cyclohexane, 0.01 mL of pure distilled water, 0.54 mL of a 25% solution of M-DEAC and 0.19 mL of a 0.25% solution of cobalt octoate in cyclohexane were charged to the glass bottles. When the cobalt octoate was added, the glass bottles were placed in an agitated polymerization bath maintained at 27°C for 40 minutes, followed by addition
20 of ethanol to stop polymerization. The polymer was recovered and dried and samples used to measure the gel content, with the results shown in Table 1.

With reference to Table 1, Experiment #1 is a control in which the cyclohexane plus water was shaken for 5 minutes which produced clearly visible particles (median much greater than 10 μm) of water in the
25 cyclohexane. The other components were added after the shaking.

In Experiment #2, the cyclohexane and water was subjected to sonification for 5 minutes in a Branson™ ultrasonic cleaner which produced a mixture of water particles in cyclohexane in which the water particles had a median particle size of less than 10 μm . The other components were added
30 after completion of the ultrasonic mixing.

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In Experiment #3, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to sonification as described above; the water particles had a median particle size of less than 10 μm . The other components were added on completion of the ultrasonic mixing.

- 5 In Experiment #4, the cyclohexane, 1,3-butadiene, butene-1 and water were subjected to shaking for 48 hours producing water particles having a median particle size of less than 10 μm . The other components were added on completion of the shaking. The gel data provided in Table 1 clearly show that the presence of water particles having a median particle
10 size of less than 10 μm resulted in the production of polymers having significantly reduced gel contents.

TABLE 1

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Experiment #	1	2	3	4
Gel (ppm)	1200	15	80	95
	1540	28	56	82
	1010	32	110	100
	1610	26	75	73
	-	30	100	-
Average Gel (ppm)	1340	26	84	87

20 EXAMPLE 2

- Using the procedure and components described in Example 1, polymerizations were undertaken in which the cyclohexane, 1,3-butadiene, butene-1, water and M-DEAC were mixed by shaking for a period ranging from 0 to 30 minutes. The other components were added on completion of
25 the shaking. The gel results shown in Table 2 show that when the median

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particle size is reduced less than 10 μm , the gel content of the polymer is significantly reduced.

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TABLE 2

Shaking Time (min)	Water Particle Size (μm)	Gel (ppm)
0	-	2950
5	-	1680
10	-	863
15	-	520
20	-	120
25	< 10	50
30	< 10	38

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EXAMPLE 3

Using the procedure described in Example 1, the following experiments were undertaken. 110 g of cyclohexane and 0.011 mL of water was subjected to sonification for 5 minutes producing a mixture containing particles of water having a median particle size of less than 10 μm . Following this, 80 g of 1,3-butadiene, 2.0 mL of a 20% solution of 1:3 cyclooctadiene in cyclohexane, 60 g of butene-1, 1.25 mL of a 12% solution of diethyl aluminum chloride in cyclohexane and 0.2 mL of a 0.25% solution of cobalt octoate in cyclohexane were added and the contents immersed in an agitated water bath at 27°C for 40 minutes. After stopping the polymerization, the polymer was recovered and the gel content was determined to be 120 ppm. In a control experiment, the same procedure was followed except that instead of being sonified, the cyclohexane and water

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was mixed by shaking. The water particles were found to have a median particle size of greater than 10 μm . The resulting polymer was found to have a gel content of greater than 3000 ppm.

- 5 All publications, patents and patent applications referred to herein are incorporated by reference in their entirety to the same extent as if each individual publication, patent or patent application was specifically and individually indicated to be incorporated by reference in its entirety.

What is claimed is:

1. A process for the production of cis-1,4-polybutadiene having a low level of gel content, the process comprising the step of polymerizing 1,3 butadiene in the presence of a catalyst and a polymerization diluent, the polymerization diluent comprising an organic solvent and water particles having a median particle size less than or equal to about 10 μm .
2. The process defined in claim 1, wherein the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 8 μm .
3. The process defined in claim 1, wherein the water is present in said polymerization diluent as particles having a median particle size in the range of from about 0.5 μm to about 6 μm .
4. The process defined in claim 1, wherein the water is present in said polymerization diluent as particles having a median particle size in the range of from about 1 μm to about 5 μm .
5. The process defined in any one of claims 1-4, wherein the organic solvent is selected from the group comprising an aliphatic compound, an aromatic compound and mixtures thereof.
6. The process defined in claim 5, wherein the aliphatic compound is selected from a saturated hydrocarbon, an unsaturated hydrocarbon and mixtures thereof.
7. The process defined in claim 6, wherein the saturated hydrocarbon is selected from the group comprising C₄-C₁₀ aliphatic hydrocarbon, a C₅-C₁₀

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cyclic aliphatic hydrocarbon, a C₆-C₉ aromatic hydrocarbon, a C₂-C₁₀ monoolefinic hydrocarbon and mixtures thereof.

8. The process defined in claim 7, wherein the C₄-C₁₀ aliphatic hydrocarbon is selected from the group comprising butane, pentane, hexane, heptane, octane and mixtures thereof.

9. The process defined in claim 7, wherein the C₂-C₁₀ monoolefinic hydrocarbon is selected from the group comprising butene-1, pentene-1, hexene-1 and mixtures thereof.

10. The process defined in claim 7, wherein the C₅-C₁₀ cyclic aliphatic hydrocarbon is selected from the group comprising unsubstituted cycloalkanes, methyl substituted cycloalkanes, ethyl substituted cycloalkanes and mixtures thereof.

11. The process defined in claim 7, wherein the C₅-C₁₀ cyclic aliphatic hydrocarbon is selected from the group comprising cyclopentane, cyclohexane, cyclooctane and mixtures thereof.

12. The process defined in claim 7, wherein the a C₆-C₉ aromatic hydrocarbon is selected from the group comprising benzene, toluene, xylene and mixtures thereof.

13. The process defined in any one of claims 1-4, wherein the organic solvent comprises a mixtures of cyclohexane and butene-1.

14. The process defined in any one of claims 1-13, wherein polymerization diluent further comprises a polymerization modifier selected from the group comprising C₂-C₁₈ non-conjugated dienes, C₆-C₁₂ cyclic dienes and mixtures thereof.

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15. The process defined in claim 14, wherein the polymerization modifier is selected from the group comprising 1,2-butadiene, 1,3-cyclooctadiene, 1,5-cyclooctadiene and mixtures thereof.

16. The process defined in any one of claims 1-15, wherein the catalyst comprises a substantially anhydrous cobalt salt and an organo-aluminum halide compound.

17. The process defined in claim 16, wherein the substantially anhydrous cobalt salt comprises a compound having the formula CoA_m , wherein A is selected from a monovalent anion and a divalent anion, and m is 1 or 2.

18. The process defined in claim 17, wherein the anion is derived from a $\text{C}_6\text{-C}_{12}$ organic acid.

19. The process defined in claim 17, wherein the anion is selected from the group comprising an acetylacetonate, an acetate, a hexanoate, an octoate, an oxalate, a tartrate, a stearate, a sorbate, an adipate and a naphthenate.

20. The process defined in claim 16, wherein the substantially anhydrous cobalt salt comprises cobalt octoate.

21. The process defined in any one of claims 16-20, wherein the organo-aluminum halide compound comprises a compound having the formula:



wherein: R is a $\text{C}_2\text{-C}_{12}$ alkyl group, X is a halogen and $p+q$ is 3.

22. The process defined in any one of claims 16-20, wherein organo-aluminum halide compound is selected from the group comprising a dialkyl

aluminum chloride compound, an alkyl aluminum sesquichloride compound and mixtures thereof.

23. The process defined in any one of claims 16-20, wherein the organo-aluminum halide compound is selected from:

(I) a mixture of: (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride and (b) an organo aluminum compound of formula R_3Al wherein R is C_8-C_{12} alkyl group; and

(II) an alkyl aluminum chloride wherein the alkyl group has 8 to 12 carbon atoms.

24. The process defined in any one of claims 16-20, wherein the organo aluminum halide comprises a mixture of: (a) an alkyl aluminum chloride selected from diethyl aluminum chloride and ethyl aluminum sesquichloride and (b) an organo aluminum compound of formula R_3Al wherein R is C_8-C_{12} alkyl group.

25. The process defined in any one of claims 23-24, wherein the organo aluminum compound of formula R_3Al is present in an amount of 0 to 1 percent by weight of the mixture.

26. The process defined in any one of claims 23-24, wherein the organo aluminum compound of formula R_3Al comprises tri-octyl aluminum.

27. The process defined in claim 16, wherein the substantially anhydrous cobalt salt comprises cobalt octoate and the organo-aluminum halide compound comprises a mixture of diethyl aluminum chloride and tri-octyl aluminum

28. The process defined in claim 27, wherein the molar ratio of cobalt octoate to the total of diethyl aluminum chloride plus tri-octyl aluminum is from about 1:15 to about 1:30.
29. The process defined in claim 27, wherein the molar ratio of chlorine in diethyl aluminum chloride to the total aluminum in diethyl aluminum chloride plus tri-octyl aluminum is from about 0.7:1 to about 0.95:1.
30. The process defined in any one of claims 1-29, wherein the water is mixed with the polymerization diluent by a mechanical method.
31. The process defined in any one of claims 1-29, wherein the water is mixed with the polymerization diluent by sonic treatment.
32. The process defined in any one of claims 1-31, wherein the polymerization temperature is in the range of from about 5° to about 40°C.

INTERNATIONAL SEARCH REPORT

International Application No

91/CA 99/00804

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F136/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 109 082 A (MATSUDA TERUHIKO ET AL) 28 April 1992 (1992-04-28) column 3, line 56 - line 62; claims	1-30, 32
X	SMIRNOVA L V ET AL: "BUTADIENE POLYMERIZATION WITH A COBALT SALT-DIISOBUTYLALUMINUM CHLORIDE-WATER CATALYTIC SYSTEM AT LOW TEMPERATURE" POLYMER SCIENCE: SERIE A, US, INTERPERIODICA, vol. 38, no. 3, page 274-278 XP000591727 ISSN: 0965-545X abstract; page 277, left column, lines 10-13 and lines 43-46	1-30, 32

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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Humbeeck, F

INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 258 924 A (SHELL INT RESEARCH) 9 March 1988 (1988-03-09) claim 1 -----	31

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/CA 99/00804

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